

COMPLEX INDIGENOUS ORGANIC MATTER EMBEDDED IN APOLLO 17 VOLCANIC BLACK GLASS SURFACE DEPOSITS. K. L. Thomas-Keptra¹ (kathie.thomas-keptra-1@nasa.gov), S. J. Clemett¹, D.K. Ross¹, L. Le¹, Z. Rahman¹, D.S. McKay², E.K. Gibson², and C. Gonzalez¹; ESCG at NASA/JSC, Mail Code JE23, Houston, TX 77058; ²ARES, NASA/JSC, Mail Code KR, Houston, TX 77058.

Introduction: Papers presented at the first Lunar Science Conference [1] and those published in the subsequent Science *Moon Issue* [2] reported the *C* content of Apollo 11 soils, breccias, and igneous rocks as ranging from ~50 to 250 parts per million (ppm). Later Fegley & Swindle [3] summarized the *C* content of bulk soils from all the Apollo missions as ranging from 2.5 (Apollo 15) to 280 ppm (Apollo 16) with an overall average of 124 ± 45 ppm. These values are unexpectedly low given that multiple processes should have contributed (and in some cases continue to contribute) to the lunar *C* inventory. These include exogenous accretion of cometary and asteroidal dust, solar wind implantation, and synthesis of *C*-bearing species during early lunar volcanism. We estimate the contribution of *C* from exogenous sources alone is ~500 ppm, which is ~4× greater than the reported average.

While the assessment of indigenous organic matter (OM) in returned lunar samples was one of the primary scientific goals of the Apollo program, extensive analysis of Apollo samples yielded no evidence of any significant indigenous organic species. Furthermore, with such low concentrations of OM reported, the importance of discriminating indigenous OM from terrestrial contamination (*e.g.*, lunar module exhaust, sample processing and handling) became a formidable task. *After more than 40 years, with the exception of CH₄ [5-7], the presence of indigenous lunar organics still remains a subject of considerable debate.* We report for the first time the identification of arguably indigenous OM present within surface deposits of black glass grains collected on the rim of Shorty crater during the Apollo 17 mission by astronauts Eugene Cernan and Harrison Schmitt.

Procedure and Results: Preparation of lunar samples 74220, 186 was discussed in detail in [8]. Our analysis sequence was as follows: optical microscopy, UV fluorescence imaging, μ -Raman, FESEM-EDX imaging and mapping, and FETEM-EDX imaging and mapping of a Focused Ion Beam (FIB) extracted section. Prior to FESEM analysis, a *Pt* surface coating ~1 nm thick was applied to enable imaging and chemical characterization of elements including *C*. We observed *C*-rich regions of interest (ROI) on three different volcanic glass beads. Each ROI was several μm^2 in size and fluoresced when exposed to UV illumination. Using FESEM imaging and EDX analysis, the largest ROI measured ~3×6 μm and was located on an edge of a rectangular plateau situated upon the uppermost surface of a glass bead designated as #1 (ROIs from beads

2 & 3 will not be discussed here). Mineral grains, up to ~400 nm in size, enriched in *Ti* and *O* with minor *Al*, consistent with rutile, and grains composed primarily of *Si*, *Al*, and *O*, consistent with glass, were embedded within the carbonaceous matter (Fig.1). Element distribution maps showed regions enriched in *Na* and *Fe* overlap some of the *C*-rich ROI. Since these element patterns do not highlight discrete grains within the ROI, they may be due in part to secondary X-ray fluorescence of underlying matrix minerals. A curved *Si*-rich filamentous feature emanating from the plateau surface covered one of the edges of the ROI indicating it was entrapped when material on the plateau surface flowed when in molten or semi-molten form (Fig. 1). Hence, the ROI was attached to the surface either during a fire-fountaining event and subsequent cooling or during impact after formation. In either case, the spatial association between the ROI and the glass and the embedded mineral grains, consistent with minerals found on the moon, indicates the ROI is arguably indigenous and therefore is not the result of anthropogenic contamination. Heterogeneous distribution of *C*-rich matter in the ROI was confirmed by element mapping (Fig. 1) and EDX spectra of discrete regions in which *C* abundances ranged from ~2 to 8× above background. We performed μ -Raman spectroscopy on this ROI which showed D, G and their second order bands consistent with carbonaceous matter and other bands noting the presence of spatially associated mineral phases, including olivine and ilmenite. The G peak center varied from 1571.7 to 1587.6 cm^{-1} with the intensity ratio (I_D/I_G) ranging from 0.82 to 1.36 and G_{FWHM} ranged from 114.2 to 127.3. All of these observations, including the decrease in the G peak center location from ~1600 cm^{-1} , I_D/I_G values < 2, and increasing dispersion of the G peak compared to standards, indicate the presence of amorphous *C* [9]. Based on work by [10] describing the interpretation of Raman spectra of *C*-bearing materials, our Raman spectra indicate this ROI contains an intimate mixture of amorphous and nanocrystalline carbonaceous matter composed of disordered sp^2 -bonds consistent with a loss of aromaticity compared to that of perfect graphite. The aromatic domain size, L_a , ranges from ~1.3 to 1.6 nm. If we assume a benzene (C_6H_6) ring diameter of 0.28 nm, the OM is composed of 5 to 6 C_6H_6 rings in diameter equivalent to a total area of ~30 rings corresponding to ~80-100 *C* atoms. This observation indicates the carbonaceous matter is highly disordered. Hence, for the first time, indigenous OM observed on returned

lunar samples is consistent with kerogen or kerogen-like OM.

A FIB section $\sim 25 \times 19 \mu\text{m}$ was extracted from the largest C-rich ROI located on bead #1 (Fig. 2). High resolution EDX element maps show the amorphous C-bearing layer contains major O and Ca with lesser amounts of Mg and Si, occasional Al, and minor K and Fe. The O distribution patterns indicate the OM contains O and is therefore inconsistent with graphite, which was reported previously in Apollo sample 72255 in the form of discrete blebs and whiskers [11]. Furthermore, we did not observe the layered, planar structure of graphite in which the distance between each plane of C atoms is 0.34 nm -- easily discernable using TEM. The origin of Ca is ambiguous but may represent the presence of an amorphous, calcite-like phase. Mg, Si and Al are present as bands and/or hotspots in the C-rich region; lack of long range order indicates these elements are present as a proto-crystalline or an amorphous/glass phase. Hotspots enriched in Ti indicate the presence of poorly crystallized domains consistent with rutile or a rutile precursor; those enriched in Fe correspond to a metal or poorly oxidized Fe-bearing phase. In one case, a grain composed of Fe-Ni metal is identified where the hotspot for Fe corresponds with that for Ni.

Discussion & Conclusion: We have identified for the first time arguably indigenous lunar OM composed of a mixture of nanophase mineral grains and disordered, kerogen-like OM. Texturally this resembles the carbonaceous matter present in carbonaceous chondrites and IDPs. While primarily composed of volcanic pyroclastic droplets, sample 74220, 186 has been slightly reworked by micrometeorites and space weathering. Therefore, the source of the OM could be from the pyroclastic eruption which formed the glass droplets and/or been added during reworking of this soil sample. Future investigations of double drive tubes 74001 and 74002, which have nearly no lunar surface reworking below a few cm, should help to constrain whether the C-rich material is indigenous to the original volcanic pyroclastic ash deposits or was added during regolith reworking.

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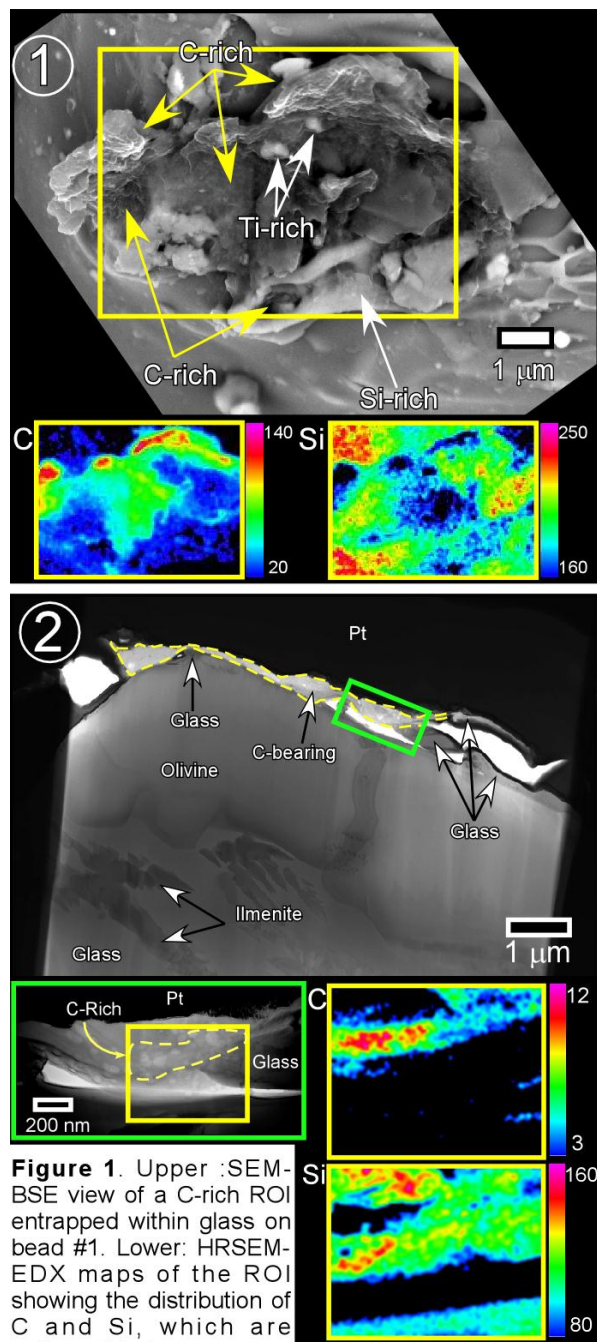


Figure 1. Upper :SEM-BSE view of a C-rich ROI entrapped within glass on bead #1. Lower: HRSEM-EDX maps of the ROI showing the distribution of C and Si, which are anticorrelated.

Figure 2. Upper: HRTEM/dark field view of the upper part of the FIB section extracted from the center of the C-rich ROI in Fig. 1. Location of the OM is highlighted by the dashed yellow line. ROI (green box) is enlarged in view at the lower left; yellow box designates the region mapped. Lower right: HRTEM-EDX maps showing the distribution of C and Si indicating the C-rich ROI is an intimate mixture of OM and Si-rich glass.